

PATENT SPECIFICATION

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NO DRAWINGS

- (21) Application No. 3434/70 (22) Filed 23 Jan. 1970
 (23) Complete Specification filed 11 Jan. 1971
 (44) Complete Specification published 21 Nov. 1973
 (51) International Classification C08G 17/015 // 33/20; C07D 105/06;
 C07F 9/28
 (52) Index at acceptance
 C3R 3D13 3D2E 3N1 3P4 7W1 7W2 7W3 7W4 7W5
 7W6 7W8 7W9 7WX
 C2J 1
 C2P 3B11A 3B12B 3B14A 3B14B 3B20 3B21 5B 7
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(54) PRODUCTION OF AROMATIC POLYESTERS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of highly polymeric polyesters of aromatic dicarboxylic acids and dihydric alcohols.

Highly polymeric polyesters of aromatic dicarboxylic acids and dihydric alcohols are known to be useful thermoplastic materials capable of conversion to films, fibres and moulded articles having a desirable combination of physical and chemical properties. Examples of such polyesters are those prepared, for example, from terephthalic acid or 1,2-di(p-carboxyphenoxy)ethane and ethylene glycol or butane-1,4-diol or 1,4-dihydroxymethylcyclohexane.

Many processes have been proposed for the production of these polyesters but in general they proceed via the formation of the bis(dihydric alcohol) ester of the aromatic dicarboxylic acid and the polycondensation of this intermediate to highly polymeric polyester with loss of dihydric alcohol by heating in a molten state under reduced pressure. The bis ester may be formed, for example, by reaction of the aromatic dicarboxylic acid or of an ester-forming derivative thereof, e.g. a dialkyl ester, with the dihydric alcohol, or by reaction of the dicarboxylic acid with an ester-forming derivative of the alcohol e.g. ethylene oxide of ethylene carbonate in the case of ethylene glycol. The process of reacting the acid with the dihydric alcohol is generally referred to as direct esterification while reacting a di-ester of the acid with the dihydric alcohol is generally referred to as trans-esterification.

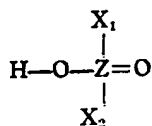
Both the process of forming the intermediate and its conversion to highly polymeric polyester by polycondensation are generally aided by the use of catalysts which are generally metals or derivatives thereof. In most conventional processes, different catalysts are used for the preparation and polycondensation. In accordance with the present invention we provide a process using a novel class of catalyst for the polycondensation and in many cases the same catalyst may also be used satisfactorily in the preliminary trans-esterification reaction to produce the intermediate.

So as not to modify, dilute or lose the highly desirable characteristic properties of the highly polymeric polyesters of dihydric alcohols and aromatic dicarboxylic acids, it is usually preferred that the polycondensable material consists substantially entirely of one or more bis(dihydric alcohol) esters of aromatic dicarboxylic acids. However, the presence of a small concentration of other polycondensable material may be tolerated, if desired, for example to improve dyeability. For example, up to about 5 mole % of the dihydric alcohol moiety in the bis ester or esters may be replaced by at least one other polycondensable dihydroxy compound and/or up to about 5 mole % of the aromatic dicarboxylic acid moiety may be replaced by at least one other dicarboxylic acid. Up to about 5 mole % of the polycondensable mixture may also consist of other mono- or polyfunctional material, if desired, e.g. monohydric alcohols and/or their esters with the dicarboxylic acids, amine and/or diamines and/or their

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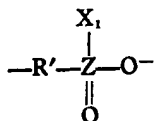
amides with the dicarboxylic acids, aminoalcohols and/or their condensation products with the dicarboxylic acids, and/or aminoacids, hydroxy acids, lactams and/or lactones and/or their condensation products with the dicarboxylic acids and/or dihydric alcohols. However, it is usually preferred that at least 85 mole %, and preferably at least 95 mole %, of the polycondensable mixture consists of bis(dihydric alcohol) ester of aromatic dicarboxylic acid.

Thus, according to the present invention, we provide a process for the production of polyesters by the polycondensation of polycondensable material at least 85 mole % of which consists of at least one bis(dihydric alcohol) ester of an aromatic dicarboxylic acid in which said polycondensation is effected in the presence, as sole essential catalyst, of at least one simple or polymeric compound containing at least one metal atom attached to at least one anionic ligand, the remaining co-ordination and valency requirements of the metal atom being satisfied by one or more other ligands, the said anionic ligand being the anion of an acid having the structure I,



I

where X_1 is $-R$ or $-OR$, and X_2 is R or a group of structure II,



II

where R is a monovalent hydrocarbyl group or substituted derivative thereof, R' is a divalent hydrocarbon group or diether group, or substituted derivative thereof, and Z is a Group Vb element having an atomic number greater than 7.

Examples of R are alkyl, aralkyl, aryl and alkaryl groups where alkyl includes cycloalkyl. Preferably R has 1 to 8 carbon atoms, e.g. as in methyl, ethyl, isomeric propyl, isomeric butyl, hexyl, cyclohexyl, octyl, phenyl, benzyl and tolyl. However, while it is preferred that R contains not more than eight carbon atoms, the presence in R of more than eight carbon atoms, e.g. as in decyl, dodecyl and naphthyl, is not excluded. One or more of the hydrogen atoms in R may be replaced, if desired, by other monovalent atoms or groups, e.g. halide, $-NR^2R^3$, $-NO_2$, $-OOCR^2$, $-COOR^2$, $-COR^2$, $-OR^2$, $-SO_2OR^2$ or $-OSO_2R^2$ where each of R^2 and R^3 is hydrogen or a monovalent hydrocarbon radical, e.g. having 1 to 6 carbon atoms. It may be found preferable that the substituted groups (if any) are free of Zerewitinoff hydrogen if reaction of the catalyst with the polycondensable mixture is to be avoided.

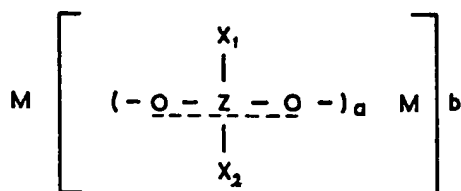
Examples of R' are alkylene groups and dioxyalkylene groups having from 1 to 8 carbon atoms. Preferably R' is methylene or 1,2-ethane.

Preferably, Z is phosphorus or, less preferably, arsenic but the use of the heavier elements of Group Vb is not excluded.

The compounds may be simple or polymeric and the polymeric compounds may be linear, branched or reticulated. In some cases the ligand I is attached to a single metal atom, but more often, the ligand behaves as a bidentate ligand joining two metal atoms. In this case it is usual for several metal atoms to be joined by a series of bidentate catenating ligands I forming dimeric, oligomeric or polymeric species. Thus the compound may be homopolymeric or copolymeric and in the latter case the nature of the metal atom and/or of the monovalent anionic bidentate catenating ligand may vary from unit to unit in the repeat units. Where adjacent metal atoms are linked together by more than one catenating ligand, the catenating ligands within each repeat unit may be the same or different and any additional catenating ligands other than the first may be other than of the kind specified. In general, it is preferred that the polymeric compounds are soluble in the polycondensable mixture and for this reason the essentially linear polymers are preferred.

It is much preferred that the compound for use as a catalyst in accordance with our invention is such that the molecule contains at least two metal atoms and that each

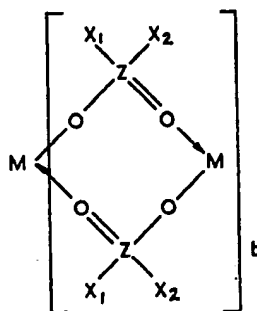
is linked to its neighbour by a centenating monovalent anionic bidentate ligand as specified above. In other words, the compound preferably contains repeat units of the structure III,



III

where Z, X₁ and X₂ have the possibilities and preferences described above, each M represents a metal atom and the metal atoms may be the same or different, the dotted line represents a delocalised charge, a is a positive whole number between 1 and 4, and b is a positive integer which may be 1 or more, and may be very much greater than 1; e.g. 10, 50 or even higher. Thus, simple compounds, oligomers and low and high polymers are envisaged, e.g. having a number average molecular weight of 5000 or even greater. However best yields of polyester are usually obtained using materials of molecular weight of 4000 or less.

While a structure III may be one, two, three or four, it is most preferably two. In other words, the compounds preferably are of the kind which contain the structure IV,

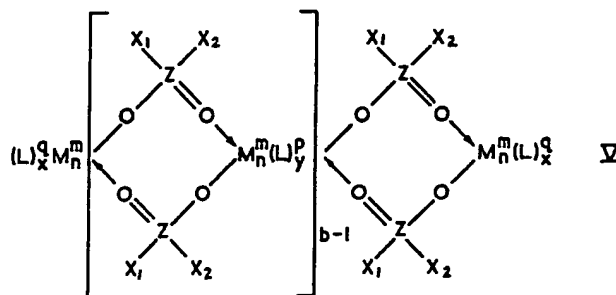


IV

and may be monomeric, oligomeric or polymeric.

In structures III and IV, each M may be any suitable metal atom and may have associated therewith one or more other ligands, depending upon its outstanding valency and co-ordination requirements. Thus, for example, where the compound is of the preferred kind containing the structure IV, and b is one, each M atom has n-2 further co-ordination sites available where n is its co-ordination number. Where b is greater than one, each intra-chain M (that is an M which is not at the end of a chain) has n-4 further co-ordination sites available. The total charge on the ligands associated with these extra co-ordination sites will depend upon the valency of the metal atom. Thus, where b is one the total charge of the ligand or ligands associated with the additionally available co-ordination sites on each metal atom M will be m-1 where m is the valency of the metal atom. Where b is greater than one, the total charge of the ligand or ligands associated with the additionally available co-ordination sites on each intra-chain metal atom M will be m-2.

Thus, the preferred compounds containing the structure IV may be represented in full by the structure V below.



where each M is a metal atom having a valency of m and a co-ordination number of n, and the metal atoms may be the same or different, each L represents a neutral or anionic mono or polydentate ligand, x and y represent the total denticity of the ligand or ligands attached to each metal atom such that x equals n-2 and y equals n-4, p and q represent the total charge over the ligand or ligands attached to each metal atom such that q equals m-1 and p equals m-2, each X₁ is —R or —OR and each X₂ is —R where R is preferably a monovalent hydrocarbyl group, preferably containing 1 to 8 carbon atoms, but may also be a substituted derivative thereof, each Z is an atom of a Group Vb element having an atomic number greater than 7 and is preferably phosphorus or arsenic, and b is a positive whole number.

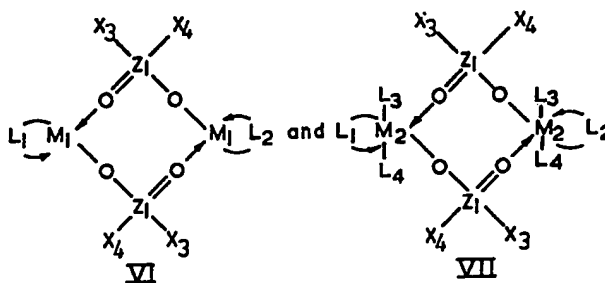
The ligands attached to the metal atoms may be neutral or mono- or polyvalent anionic and mono- or polydentate. In the case of polydentate ligands, they may bridge adjacent metal atoms and may produce a branched or reticulated structure by linking adjacent chains.

Examples of M include

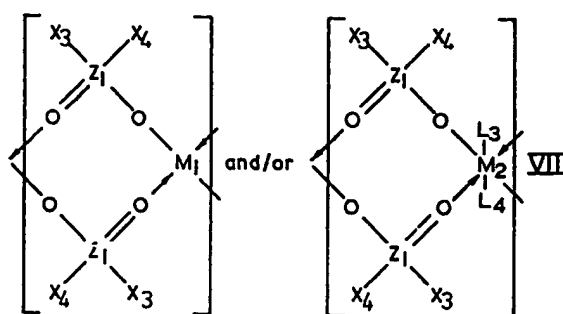
- (a) divalent tetracoordinate, e.g. Ca²⁺, Zn²⁺, Mn²⁺, Co²⁺, Cd²⁺, Pb²⁺
- (b) divalent hexacoordinate, e.g. Mn²⁺
- (c) trivalent hexacoordinate, e.g. Mn³⁺, Ti³⁺, La³⁺, Al³⁺, Sb³⁺
- (d) tetravalent hexacoordinate e.g. Sn⁴⁺
- (e) tetravalent octacoordinate e.g. Ce⁴⁺, Th⁴⁺, Ti⁴⁺, Zr⁴⁺.

Examples of ligands other than the specified catenating ligands that may be associated with the metal atoms in the compounds include monodentate neutral ligands, e.g. CO, H₂O, NH₃, and molecules having the structure R¹R²R³Y or R¹R²R³Y:O where each R¹, R² and R³ is a monovalent hydrocarbyl or hydrocarbyloxy group, preferably having one to eight carbon atoms e.g. as in methyl, ethyl, propyl, butyl, hexyl, octyl, phenyl, tolyl, benzyl, methoxy, ethoxy, propoxy, butoxy and phenoxy, and Y is phosphorus or arsenic; monodentate anionic ligands, e.g. halide especially chloride, nitrate, nitrile, hydroxyl, thiocyanate, cyanate and isocyanate; neutral bidentate e.g. ethylene diamine; and monovalent anionic bidentate, e.g. anions of monocarboxylic acids, anions of enolisable compounds such as acetylacetonates or anions of bisphosphinates or bisarsonates.

Specific examples of compounds that may be used as catalysts in accordance with this invention are simple compounds having the structures VI and VII.



and polymeric and copolymeric compounds having repeat units of the structure VIII.

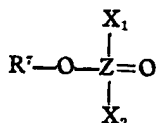


where each M_1 is Ca, Zn, Mn or Co, each M_2 is Ti or Zr, each Z_1 is P or As, each X_3 is a monovalent hydrocarbon group having from 1 to 6 carbon atoms, e.g. methyl, ethyl, propyl, isopropyl, butyl, amyl, hexyl, cyclohexyl or phenyl, each X_4 is a monovalent hydrocarbon group having from 1 to 6 carbon atoms, an alkoxy or cycloalkoxy group having from 1 to 6 carbon atoms or phenoxy, L_1 and L_2 are monovalent anionic bidentate ligands selected from carboxylate, acetylacetonate and anions of acids having the structure I above where Z is P or As, each R is a monovalent hydrocarbon group having from 1 to 8 carbon atoms, and L_3 and L_4 are monovalent anionic monodentate ligands selected from carboxylate, acetylacetonate, hydrocarbyloxy having from 1 to 8 carbon atoms and anions having the structure I above where Z is P or As, each R is a monovalent hydrocarbon group having from 1 to 8 carbon atoms, or L_3 and L_4 together form a bis phosphonate or bis phosphinate ligand.

The catalysts of the invention may be prepared in a number of ways and it has been our experience that the manner in which they are prepared has some effect upon their catalytic efficiency in the process of the invention.

One method of preparing the catalyst, which is especially suitable for forming those in which M is divalent tetracoordinate, is to react a soluble simple or complex salt of the metal, e.g. the metal di(acetylacetonate) or metal acetate, with an acid having the structure I in an anhydrous organic liquid which is a solvent for both the reagents, and with or without a basic catalyst, e.g. pyridine. The product may then be recovered, for example by crystallisation, volatilisation of the solvent, centrifugation or filtration, depending on whether or not the organic liquid is a solvent for the polymer. The reaction may proceed at room temperature, preferably with agitation, but heat may be applied, if desired, e.g. up to the refluxing temperature of the solvent. Examples of solvents are aliphatic alcohols, e.g. ethanol, aromatic hydrocarbons, e.g. benzene and toluene, and ketones, e.g. acetone. The molecular weight of the compound produced will depend upon the molar ratio of the reagents, becoming greater as the ratio of metal compound to acid approaches 1:2.

Another method of preparing the catalyst, which is also suitable for forming those in which M is divalent tetracoordinate, is to react directly the metal salt (simple or complex) with an ester of structure:



where R' is monovalent hydrocarbyl, for example, an alkyl group containing from 1 to 3 carbon atoms. This reaction may require more forcing conditions, for example heating the reagents at elevated temperatures of at least 120°C and preferably 180°C or even higher. A solvent may be used if desired and examples of suitable solvents are ethylene glycol and its monomethyl ether. The polymeric products of this reaction generally appear to be more effective polycondensation catalysts than those of the first and for this reason this process is preferred. We have found that this method is effective.

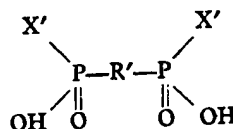
tive for all possibilities of X_1 and X_2 . It appears that irrespective of the total number of hydrocarbyloxy groups attached to the Z atom, only one takes part in the synthetic reaction to form the catalyst.

Another very effective method is to heat the metal salt and the acid of structure I until fusion occurs. Possibly this method is advantageous because, in general, polymers of molecular weight less than 4000 are obtained. Yet another method involves an interfacial technique wherein a solution of the metal salt in one solvent is vigorously mixed, e.g. in a high speed stirrer, with a solution of the acid of structure 1 in a second solvent immiscible with the first. Examples of immiscible solvent pairs are water and benzene, toluene, xylene or carbon tetrachloride.

Another method, which is especially suitable for complex compounds of trivalent hexacoordinate metals, comprises heating a mixture of (a) a chelate complex consisting of the metal and a bidentate monovalent anionic ligand with (b) the acid of structure I, e.g. in a molar ratio of 1:2, at a temperature sufficient to volatilise the acid corresponding to the anionic ligand of the chelate complex. Alternatively, the reaction may be effected in a high boiling solvent, e.g. a biphenyl or chlorinated biphenyl.

A still further method, also especially applicable to trivalent hexacoordinate metals, involves two steps: first reacting one mole of a salt of the metal in its divalent state with two moles of an anion of the acid of structure I, then oxidising the intermediate product so formed in the presence of one neutral and one anionic ligand. The first step may be effected with the reagents as a slurry in an aqueous alcoholic medium or in an organic alcoholic solvent. There is no need to isolate the intermediate. Oxidation may be effected, for example, by oxygen, hydrogen peroxide, chlorine or chloride ion. Air may also be used for oxidation, if desired.

Yet another method, especially applicable to the production of some tetravalent hexacoordinate titanium compounds, comprises reacting the metal tetraalkoxide with a substantially equimolar amount of a P,P-di-substituted alkylene diphosphinic acid of structure



X

where each X' is monovalent hydrocarbon or hydrocarbyloxy and R' is alkylene, to obtain the dialkoxy-titanium diphosphinate and using this alone, or further reacting this compound with an acid of structure I, e.g. in the molar ratio of 1:2. The first reaction may be carried out at room temperature or at elevated temperatures up to e.g. 135°C and preferably by adding the diphosphinic acid to a solution of the titanium alkoxide in, for example, benzene, toluene, chloroform or xylene. The subsequent reaction is preferably also carried out in a solvent, e.g. benzene or toluene. Temperatures of 60 to 150°C are preferred.

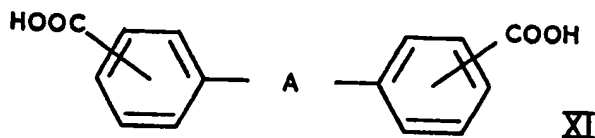
Not all the above described processes may be applicable to the production of any particular catalyst but in general each of our specified catalysts may be prepared by one or more of the above described processes or obvious modifications thereof.

In accordance with our invention, these catalysts may be used to aid the polycondensation to highly polymeric polymer of polycondensable mixtures consisting mainly or entirely of bis(dihydric alcohol) esters of aromatic dicarboxylic acids. It is preferred that the metal atoms in the catalyst are of metals in Groups II, III, IV or VII or cobalt. Catalysts wherein M is Zn^{2+} are particularly preferred for their activity and ability to yield highly polymeric products of good colour; those wherein M is Mn^{2+} and Ti^{4+} are also very active. An especially preferred group of catalysts are those containing both Zn^{2+} and Co^{2+} in the simple or polymeric molecule.

In some cases, the complex compounds may also be used as catalysts for the production of the bis(dihydric alcohol) ester of the aromatic dicarboxylic acid by transesterification. Whether or not this is possible depends largely on the metal used in the catalyst. Zinc, manganese, sodium, calcium, titanium, aluminium, cobalt, tin, iron, lanthanum, lead and cadmium are capable of catalysing ester interchange as well as polycondensation. It is anyway desirable that the complex compound is added to the polycondensation mixture before or at the latest just after the commencement of the polycondensation reaction, e.g. before the polymer has attained an intrinsic viscosity of 0.2.

According to a further aspect of the invention, therefore, we provide a process for the production of polyesters in which a bis(dihydric alcohol) ester of an aromatic dicarboxylic acid is prepared by ester interchange between a dialkyl ester of the aromatic dicarboxylic acid and a dihydric alcohol, said ester interchange being catalysed by the catalyst hereinbefore described, the metal being selected from zinc, manganese, calcium, sodium, titanium, aluminium, lanthanum, lead, cobalt, iron and cadmium, and in which the bis(dihydric alcohol) ester of an aromatic dicarboxylic acid is then converted to polyester by polycondensation, the same catalyst being used in the polycondensation reaction.

The invention is especially applicable to the production of polyesters wherein the dicarboxylic acid component is at least 80 mole % terephthalic acid but other aromatic acids may also be used. Examples of other aromatic dicarboxylic acids include isophthalic acid and dinuclear dicarboxylic acids, e.g. represented by the structure XI



where A is a direct link or a divalent atom or group which is inert under present reaction conditions.

Examples of dihydric alcohols that may be used are α,ω -polymethylene glycols, especially those having the structure $\text{HO}(\text{CH}_2)_x\text{OH}$ where x is from 2 to 10 e.g. ethylene glycol and butane-1,4-diol, branched aliphatic diols e.g. 3,3,5-trimethylhexane-1,6-diol and neopentyl glycol, and alicyclic diols e.g. 1,4-di(hydroxymethyl)-cyclohexane and 2,2,4,4-tetramethyl cyclobutane-1,3-diol.

The catalyst may be used in amounts of from 0.00001 to 1% by weight of the acid component (i.e. acid, dialkyl esters thereof or bis glycol ester thereof) in the reaction mixture, the preferred concentration being in the range 0.005 to 0.2% by weight though with many titanium based catalysts 0.0001% by weight gives good results. With the use of the catalyst in these concentrations, rapid reactions may be achieved. Moreover, with the use of many of the catalysts of our invention the clarity of the polyester melt has been observed to be better than that of high molecular weight polyesters obtained from many processes using conventional catalyst systems, e.g. based on metal acetates and metal oxides. Larger amounts of the catalyst may be used if desired but any further benefit in reaction rate that is obtained may be offset by discolouration in the polyester product. With the use of much smaller amounts, little or no benefit is obtained.

Conventional reaction conditions may be used for the production of the bis glycol ester or oligomer and its subsequent polycondensation and other additives may be included before, during or after the reactions, e.g. for delustring, stabilising, pigmenting and/or otherwise modifying the high molecular weight polyester product.

The invention is now illustrated by the following Examples in which all parts are expressed as parts by weight.

EXAMPLES.

A. Preparation of Reagents General Procedure

All melting points were carried out on a Kofler block melting point apparatus and mean molecular weights were calculated by vapour pressure osometry. Volatile distillates were analysed by mass spectrometry, on a MS9 instrument, and by g.l.c. on a Perkin-Elmer F11 instrument, using a 6' porapak R column at 180°C and a flow rate of 50 mls./min. The n.m.r. spectra were run on a 220 MHz instrument. Relative viscosities were measured in an Ostwald U-tube viscometer using a 1% solution in o-chlorophenol and the intrinsic viscosities therefrom.

Cacodylic acid (dimethylarsinic acid), calcium, cadmium, chromous, cobaltous, copper, lanthanum, lead, magnesium, manganous, nickel, sodium and zinc acetates, were all Laboratory Reagents from B.D.H. Ltd. Zinc and vanadyl acetylacetonates were obtained from Koch-Light Ltd. and Alpha Inorganics, respectively. Diphenylphosphinic acid originated from Albright and Wilson Ltd., and was recrystallised from

absolute ethanol before use. Cadmium, lanthanum, ferric and manganic acetylacetonates, stannous acetate, and the other phosphorus and arsenic compounds were prepared by standard procedures.

Ethylene glycol and dimethylterephthalate were 'polyester grade'. 'DE monomer' is the product of the direct esterification of terephthalic acid with ethylene glycol.

B. Preparation of Catalyst

General Procedure

The compounds used as catalysts were prepared by one of the four following methods.

Method A: By stirring the starting materials, i.e. metal salt, and acid or ester under an inert atmosphere in absolute ethanol at reflux.

Method B: By stirring the starting materials in hot ethylene glycol, with a small nitrogen flow to remove the volatile materials.

Method C: By stirring in the absence of solvent with a small nitrogen flow to remove the volatile materials and finally evacuation.

Method D: Interfacial polymerisation in water/toluene.

The preparation of various zinc phosphinates and phosphonates is described in detail below and the preparation of other compounds is summarised in Tables I to V. Preparation of poly(zinc methylphenylphosphinate) by method A (JACS (1964) 84 3200)

Zinc acetate dihydrate (1.1 parts) and methylphenylphosphinic acid (1.56 part) were stirred vigorously for one hour in absolute ethanol (300 parts). A white solid was deposited, separated by filtration, washed three times with absolute ethanol (25 parts) and vacuum dried to give the zinc phosphinate polymer (1.15 parts, 61% yield), number average molecular weight, (\bar{M}_n) $4900 \pm 5\%$. This white solid became a glass at approximately 150°C and softened at about 195°C to give a melt from which long flexible fibres could be drawn.

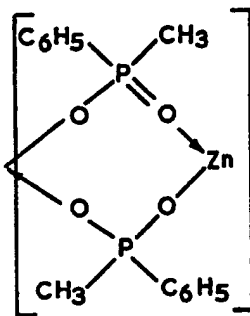
The proton n.m.r. spectrum (CDCl_3) showed a doublet at 8.63τ (P—Me) and multiplets at 2.80 and 2.40τ due to m-, p- and o-phenyl protons respectively.

Anal: Found: C, 44.17; H, 4.31; Zn, 16.4%

Calculated for $[\text{C}_{11}\text{H}_{10}\text{O}_2\text{P}_2\text{Zn}]_n$: C, 44.70; H, 4.29; Zn, 17.36%

Preparation of poly(zinc phenylmethylphosphinate) by method B

8.8 parts of zinc acetate dihydrate and 14.0 parts of methyl phenyl(methyl)phosphinate were refluxed in ethylene glycol (50 parts) under nitrogen for 3 hours in a reaction vessel fitted with a distillation unit and a nitrogen inlet positioned below the surface of the reactants. During the reaction, volatile by-products consisting of methanol, methyl acetate, some ethylene glycol and water distilled from the reaction mixture. After cooling, the solid reaction product was filtered from the glycol. It melted at 110 – 114°C and was confirmed by infra-red spectroscopy and nuclear magnetic resonance as poly(zinc phenylmethylphosphinate) believed to have the repeat unit



The molecular weight was calculated as $\bar{M}_n = 1240 \pm 10\%$.

Anal: Found C, 44.60; H, 4.35; Zn, 15.63%

Calculated for $[\text{C}_{11}\text{H}_{10}\text{O}_2\text{P}_2\text{Zn}]_n$: C, 44.70; H, 4.29; Zn, 17.36%

The reaction could also be effected in the absence of the diluent (ethylene glycol), e.g. using a temperature of 200°C .

Reaction of Zinc acetate with di-isopropyl methanephosphonate

(a) 1:1 mole ratio — Preparation of dimeric product.

Zinc acetate dihydrate (22 g, 0.1 mole) and di-isopropyl methane phosphonate (18.0 g, 0.1 mole) were reacted by method C, for one hour at 160°C. Volatile by-products (15.2 g.) were collected in a cooled receiver and g.l.c. analysis and mass spectra showed this to contain a 1:1 mixture of isopropyl acetate and isopropyl alcohol as well as the water from the hydrate. Theoretical amount of water and isopropyl acetate should have been 13.8 g; the excess weight of distillate was probably due to some phosphonate having distilled. The residue (23.5 g, 90% yield) had \bar{M}_n 530±25 and an i.r. spectrum consistent with a zinc mono-acetate mono-phosphonate dimer. The n.m.r. spectrum (in CD₃OD) showed a doublet at 8.75τ (CH₃ of isopropyl group), a doublet of 8.63τ (CH₃ on P=O), a singlet at 8.0τ (CH₃ on acetate) and a multiplet at 5.4τ (CH on isopropyl group). Peaks at 7.1τ, 2.7τ, 4.6τ and 4.8τ were due to impurities.

Anal: Found: C, 26.2; H, 5.04; P, 13.14; Zn, 22.30%

Calculated for C₁₂H₂₈O₁₀P₂Zn₂: C, 27.5; H, 4.9; P, 11.85; Zn, 25.02%

(b) 2:1 mole ratio: Preparation of poly(zinc isopropyl methanephosphonate)

Zinc acetate dihydrate (4.4 g., 0.02 mole) and di-isopropyl methanephosphonate (7.2 g., 0.04 mole) were heated as described above for the reaction with mole ratios of 1:1. The distillate (4.3 g.), was shown to consist of a mixture of isopropyl alcohol and isopropyl acetate (1:2), by g.l.c. analysis. The residue (6.4 g., 95% yield) had \bar{M}_n 2,000±120 and an i.r. spectrum consistent with a poly[zinc isopropyl methanephosphonate].

Preparation of poly(zinc diphenylphosphinate) by interfacial polymerisation (method D)

Zinc acetate dihydrate (2.195 parts) in water (100 parts) was mixed with diphenylphosphinic acid (4.4 parts) in toluene (200 parts) and the mixture agitated rapidly at room temperature for one hour. The white solid was then filtered, washed with ethanol (200 parts) and dried at 80°C.

Yield: 3 parts (60%).

C. General Procedure: Polymerisation

In most cases dimethyl terephthalate and ethylene glycol were used as the starting material and the catalyst was used for both ester interchange and polycondensation. Ester interchange was carried out in a glass vessel fitted with an efficient distillation column. Dimethyl terephthalate and ethylene glycol was charged to the vessel under a nitrogen atmosphere with the catalyst in a proportion of 480:382:0.02—0.4 g. The mixture was heated to 200°C and maintained at this temperature until distillation of the methanol had stopped. The time taken was approximately 2 hours. In certain cases, it was found that the catalyst was not effective for ester interchange, so bis-(ethylene glycol)terephthalate obtained by either direct esterification or by manganese acetate catalysed ester interchange was obtained.

Two general polycondensation procedures were used. In the first method a glass polycondensation vessel was used which was fitted with a nitrogen inlet dipping below the level of the reactants, thereby effecting agitation. There was also provision of a vacuum offtake and condensing arrangements for volatile materials.

In the second method a stainless steel autoclave was used, which was provided with a double helical metal stirrer. The bis(ethylene glycol) ester was charged to the polycondensation vessel.

Optionally at this stage, 2.4 parts of titanium dioxide were then added. The temperature was then raised to 280°C. Pressure within the vessel was then reduced to 0.5 mm of mercury absolute over a period of 30 minutes, and heating was continued for 3 hours at 280°C in the glass vessel or 1½ hours in the steel vessel. The polymeric reaction product was extruded onto chill-cast rollers and the intrinsic viscosity was measured.

Examples 1 to 26.

A series of zinc-containing catalysts were prepared by the techniques described above using various ligands containing phosphorus or arsenic. These were used for both ester interchange and polycondensation in a stainless steel autoclave. The zinc com-

pounds were mainly polymeric, with molecular weights up to about 5000. Except where indicated, the following conditions were used
 Ester interchange (EI) cycle time: 120 minutes
 Polycondensation (PC) cycle time: 90 minutes
 Delustrant: 0.5% by weight titanium dioxide added except where indicated
 Product colour: white except where indicated or colourless in the absence of titanium dioxide.

Abbreviations: Me=methyl, Et=ethyl, i-Pr = isopropyl, Ph = phenyl.
 Further details are tabulated in Table I and the notes which follow it.

TABLE I

Example No.	EI & PC Catalyst	Method of Preparation	Catalyst Weight (g.)	Intrinsic Viscosity of Polyester
1	Zn (Me,Me)Phosphinate polymer from acetate and ester at 200°C	C	0.081	0.70
2	Zn(Me,Me)Phosphinate polymer from acetate and acid	A	0.081	0.82
3	Zn(Me,Me)Phosphinate acetate dimer from acetate and ester at 200°C	C	0.069	0.74
4	Zn(Me,Ph)Phosphinate polymer from acetate and ester at 200°C	C	0.124	0.76
5	"	C	0.124	0.57
6	Zn(Me,Ph)Phosphinate polymer from acetate and acid	A	0.124	0.44
7	Zn(Me,Ph)Phosphinate polymer from acetate and ester in glycol	B	0.124	0.70
8	Zn(Me,Ph)Phosphinate prepared from acetate plus 1.8 moles of ester	C	0.124	0.63
9	As Example 8 but molar equivalents of zinc salt and ester	C	0.09	0.74

TABLE I (continued)

Example No.	EI & PC Catalyst	Method of Preparation	Catalyst Weight (g.)	Intrinsic Viscosity of Polyester
10	Zn(Me ₂ Ph)Phosphinate from acetylacetonate	C	0.124	0.77
11	Zn(Me ₂ Ph)Phosphinate polymer from acetylacetonate and acid	A	0.124	0.67
12	Zn(Ph ₂ Ph)Phosphinate polymer from acetate and ester at 200°C	C	0.163	0.57
13	Zn(Ph ₂ Ph)Phosphinate polymer from acetate and acid	D	0.041	0.58
14	Zinc ethyl methane phosphonate polymer from acetate and ester at 200°C	C	0.102	0.71
15	Zinc ethyl methane phosphonate polymer from acetate and ester at 200°C	C	0.102	0.57
16	Zinc ethyl ethane phosphonate polymer in glycol soln. (2.0 mls.)	B	0.023	0.67
17	Zinc isopropyl methane phosphonate polymer from acetate and ester at 200°C	C	0.11	0.67
18	Zinc acetate isopropyl methane phosphonate dimer	C	0.081	0.62
19	Zinc ethyl benzene phosphonate polymer from acetate and ester at 200°C	C	0.142	0.65
20	Zinc ethyl α -toluene phosphonate polymer from acetate and ester at 200°C	C	0.148	0.82
21	Zn Bisphosphonate from acetate and tetraethylmethylecnebisphosphonate	C	0.096	0.71

TABLE I (continued)

Example No.	EI & PC Catalyst	Method of Preparation	Catalyst Weight (g.)	Intrinsic Viscosity of Polyester
22	Zn/Co(Me,Ph)phosphinate polymer from acetates and ester at 200°C 10 : 1 Zn/Co	C	0.124	0.67
23	As 22 but 20 : 1 Zn/Co	C	0.124	0.74
24	Zn(Me,Me)Arsinate polymer from acetylacetone and acid at 200°C	C	0.1105	0.74
25	Zn(Me,Me)Arsinate polymer from acetate and acid	C	0.1105	0.72

NOTES ON TABLE I

5	Example No. 3	Molecular weight measurements were reasonably consistent with a dimeric catalyst.	5
10	4, 6	In Example 4 the number average molecular weight of the catalyst was 1250 whereas in Example 6 it was of the order of 5000. A higher molecular weight polyester was obtained in the former case.	10
15	5	Delustrant titanium dioxide omitted.	15
	6	Polycondensation cycle time 60 minutes.	
	7	Polycondensation cycle time 60 minutes.	
	8	Ester interchange cycle time 115 minutes. Polycondensation cycle time 60 minutes.	
	10	Number average molecular weight of catalyst $435 \pm 5\%$.	
	14	Number average molecular weight of catalyst $2500 \pm 10\%$.	
	15	Delustrant titanium dioxide omitted.	
	18	Catalyst dimeric: molecular weight $530 \pm 25\%$. Ester interchange cycle time 105 minutes.	
20	19	Ester interchange cycle time 480 minutes.	20
	21	Ester interchange cycle time 720 minutes. Product polyester slightly cream coloured.	
	22	Zinc/cobalt copolymer, from acetates in molar ratio 10 : 1.	
	23	As Example 22, but molar ratio of acetates 20 : 1	

- 24 Ester interchange cycle time 80 minutes.
 25 Ester interchange cycle time 85 minutes.
 Examples 26 to 34.
 5 A series of manganese containing catalysts were prepared by the techniques described above using various ligands containing phosphorus or arsenic. These were used as catalysts by the procedure of Examples 1 to 25.
 The manganese salt was divalent.
 Product colour was cream or white.
 Further details are tabulated in Table II and in the notes which follow it.

TABLE II

Example No.	El & PC Catalyst	Method of Preparation	Catalyst Weight (g.)	Intrinsic Viscosity of Polyester
26	Mn(Me,Me)Phosphinate polymer from acetate and acid in EtOH	A	0.166	0.85
27	Mn(Me,Me)Phosphinate polymer from acetate and ester at 200 °C	C	0.166	0.80
28	Mn(Me,Ph)Phosphinate polymer from acetate and acid in EtOH	A	0.255	0.78
29	Mn(Me,Ph)Phosphinate polymer from acetate and ester at 200 °C	C	0.1752	0.65
30	Mn(Me,Ph)Phosphinate polymer from acetylacetonate and acid in EtOH	A	0.363	0.68
31	Mn(Ph,Ph)Phosphinate polymer from acetate and ester in glycol	C	0.34	0.65
32	Manganese ethyl methane phosphonate polymer from acetate and ester at 200 °C	C	0.18	0.45
33	Mn(Me,Me)Arsinate polymer from acetate and acid at 200 °C	C	0.226	0.65
34	Mn(Ph,Ph)Phosphinate polymer from acetate and ester in glycol.	B	0.363	0.65

NOTES ON TABLE II

Example No.			
5	26	The manganese phosphinate polymer was a light pink solid, m.p. $>320^{\circ}\text{C}$, soluble in water.	5
	29	Number average molecular weight of manganese polymer: approx. 2000. m.p.: 191°C , soluble in chloroform. Polycondensation cycle time: 60 minutes.	
	30	Although a trivalent manganese salt was used for the preparation, magnetic susceptibility measurements indicated that the manganese polymer contained Mn^{2+} . Ester interchange cycle time: 140 minutes.	10
	31	Ester interchange cycle time: 180 minutes.	
	32	Polycondensation cycle time: 60 minutes.	
10	34	A repeat of Example 31 using different method of catalyst preparation.	
Examples 35 to 41.			
15	This group of Examples demonstrates the use of simple and polymeric compounds of a variety of metals. In all cases the general procedure of the previous Examples was followed and in each case the metal compound was used as both ester interchange and polycondensation catalyst, though in several cases the EI cycle time was inconveniently long.		15
20	Results are summarised in Table III.		20

TABLE III

Example No.	EI & PC Catalyst	Method of Preparation	Number Average Mol Wt. of Catalyst	Catalyst Weight (g.)	EI cycle time (mins)	PC cycle time (mins)	Intrinsic Viscosity of Polyester	Polyester Colour
35	Calcium ethyl ethane phosphinate from acetate and ester at 200°C	C	260±5%	0.66	210	90	0.38	white
36	Sodium ethyl ethane phosphinate from acetate and ester at 200°C	C	100±5%	0.32	960	90	0.5	white
37	Ti(Me ₂ Ph)Phosphinate polymer	*		0.1336	210	60	0.57	yellow
38	Al(Me ₂ Me)Phosphinate from acetylacetone and acid	A		0.163	18 hrs	90	0.68	white
39	La(Me ₂ Ph)Phosphinate from acetate and 3 moles of acid at 200°C	C		0.2092	350	90	0.5	white
40	La(Me ₂ Ph)Phosphinate acetate from acetate and 2 moles of acid at 200°C	C		0.176	300	150	0.7	slightly cream
41	Pb(Me ₂ Ph)Phosphinate	C	600±10%	0.24	130	90	0.69	yellow

*Prepared as in U.S. Patent 3,425,050.

Examples 42 to 46.

This group of Examples demonstrates the use of complexes of certain metals as polycondensation catalysts which are either ineffective or only moderately effective as ester-interchange catalysts.

In Example 42, a conventional manganese acetate (0.037% by weight based on dimethyl terephthalate) catalyst was used for ester interchange. In the remaining Examples in the group D.E. monomer was used. Polycondensation conditions were as described in the previous Examples, except that in Examples 42 and 43 the polycondensation cycle time was 120 minutes.

Results are summarised in Table IV.

5

10

TABLE IV

Example No.	PC Catalyst	Method of Preparation	Number Average Mol Wt. of Catalyst	Catalyst Weight (g.)	Intrinsic Viscosity of Polyester	Polyester Colour
42	Zr(Me ₂ Ph)Phosphinate from acetylacetone and ester	C	720 ± 5%	0.2992	0.51	white
43	Vanadyl acetylacetone (Me ₂ Ph) Phosphinate from acetylacetone and acid	C	360 ± 3%		0.5	brown
44	Al(Me ₂ Me)Phosphinate from acetylacetone and acid	A		0.163	0.65	white
45	Sb(Me ₂ Ph)Phosphinate from acetate and ester at 200°C	C	220 ± 10%	0.231	0.62	white
46	Sb(Me ₂ Ph)Phosphinate acetate from acetate and acid in EtOH	A		0.192	0.66	slightly cream

Examples 47 to 51.

In this series of Examples polycondensation was carried out by the standard procedure described above for the glass polymerisation vessel. No delutant was used. In Example 51, the catalyst was ineffective for ester interchange, so D.E. monomer was used.

Results are shown in Table V.

TABLE V

Example No.	EI & PC Catalyst	Method of Preparation	Catalyst Weight (g.)	EI cycle time (mins)	PC cycle time (mins)	Intrinsic Viscosity of Polyester	Polyester Colour
47	Fe(Me,Ph)Phosphinate from Fe ³⁺ acetylacetonate and 3 moles acid	C	0.11	180	180	0.5	yellow
48	Cobalt ethyl ethane phosphinate from acetate and acid	C	0.08	120	180	0.55	blue
49	Cd(Me,Ph)Phosphinate from acetate and ester at 200°C	C	0.023	180	180	0.57	light yellow
50	Stannous ethyl ethane phosphinate from Sn ²⁺ acetate with ester at 200°C	C	0.079	210	180	0.70	orange
51	Sn(Ph,Ph)Phosphinate from Sn ²⁺ acetate with acid in EtOH	A	0.11	*	180	0.70	dark yellow

*No EI activity.

Example 52.

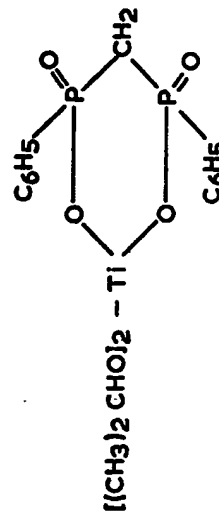
Catalyst preparation.

A titanium phosphinate polymer was prepared as follows:

5

1.8 parts of a titanium chelate

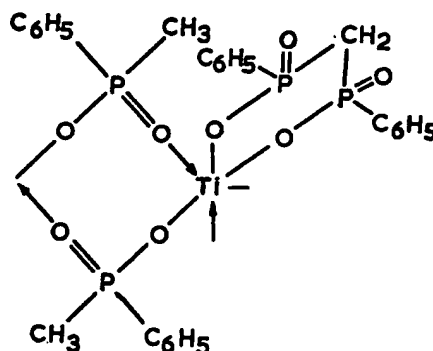
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(prepared as described in the specification of U.S. patent No. 3,403,176) and 1.22 parts of phenylmethylphosphinic acid were dissolved in 56 parts of benzene. The mixture was stirred under nitrogen for 1 hour, and then the benzene/isopropyl alcohol was removed at atmospheric pressure by distillation leaving a white polymeric product in 98% yield.

Analysis:	Calculated	[C ₂₇ H ₂₃ O ₃ P ₂ Ti]	Found
	C	49.71	48.40
	H	4.33	4.39
	Ti	7.34	7.34

The polymer is believed to be formed of repeat units having the structure

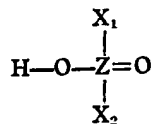


Polymerisation.

The polymerisation was as described in Example 1 but using a Pc cycle time at an absolute pressure of 0.5 mm of mercury of 2 hours. 0.0326 g of the titanium phosphinate polymer prepared as described above was used as the catalyst. The polymeric product had an intrinsic viscosity of 0.71.

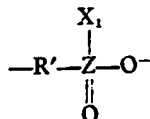
WHAT WE CLAIM IS:—

1. A process for the production of polyesters by the polycondensation of polycondensable material at least 85 mole % of which consists of at least one bis(dihydric alcohol) ester of an aromatic dicarboxylic acid, in which said polycondensation is effected in the presence, as sole essential catalyst, of at least one simple or polymeric compound containing at least one metal atom attached to at least one anionic ligand, the remaining co-ordination and valency requirements of the metal atom being satisfied by one or more other ligands, the said anionic ligand being an anion of an acid having the structure



I

where X₁ is —R or —OR, and X₂ is R or a group of structure II

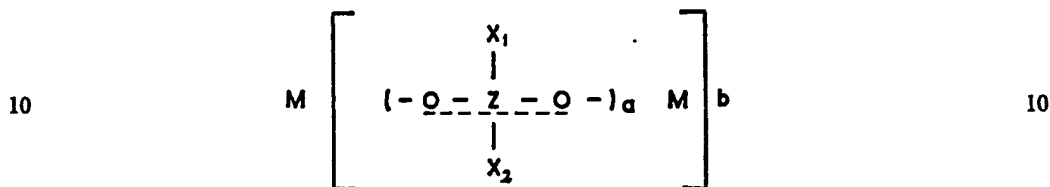


II

where R is a monovalent hydrocarbyl group or substituted derivative thereof, R' is a divalent hydrocarbon group or diether group, or substituted derivative thereof, and Z is a Group Vb element having an atomic number greater than 7.

2. A process according to claim 1 in which the catalyst is at least one simple or polymeric compound containing at least two metal atoms, each metal atom being linked to its neighbour by at least one anionic bidentate catenating ligand derived from an acid of structure 1.

3. A process according to claim 1 or claim 2 in which the catalyst is a polymer containing repeating units of the structure



where Z and X₁ and X₂ are defined as in claim 1, M is a metal atom,

a is 1 to 4

b is a positive integer.

4. A process according to any one of claims 1 to 3 in which the metal is selected from zinc, manganese, zirconium, aluminium, lanthanum, tin, and zinc/cobalt mixtures.

5. A process according to any one of claims 1 to 6 in which the catalyst is a polymeric compound having a number average molecular weight up to 4000.

6. A process for the production of polyesters in which a bis(dihydric alcohol) ester of an aromatic dicarboxylic acid is prepared by ester interchange between a di-alkyl ester of the aromatic dicarboxylic acid and a dihydric alcohol, said ester interchange being catalysed by the catalyst described in any one of claims 1 to 5, the metal being selected from zinc, manganese, calcium, sodium, titanium, aluminium, lanthanum, lead, cobalt, iron and cadmium and in which the bis(dihydric alcohol) ester of an aromatic dicarboxylic acid is then converted to polyester by polycondensation, the same catalyst being used in the polycondensation reaction.

7. A process for the production of polyesters, substantially as described in Examples 1, 6, 7, 11, 16, 18, 22, 23, 35 and 52.

8. A process for the production of polyesters substantially as described in Examples 2-5, 8-10, 12, 13, 15, 17, 19-21, 24-34, 36-51.

9. Polyesters whenever produced by processes according to any one of claims 1 to 8.

10. Fibres, films or other shaped articles formed from polyesters according to claim 9.

M. JONES,
Agent for Applicants.

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